METHOD AND APPARATUS FOR REMOVING METALS FROM METAL- SALT SOLUTIONS

Publication number: CA1180195

Publication date: 1985-01-01

Inventor: FISCHER HOLGER; RACHOR FRANK; ESNA-ASHARI MOHAMMED; PATERNOGA PAUL; DOLL MANFRED; HILLMANN GERD

Applicant: KLOECKNER HUMBOLDT DEUTZ AG

Classification:

- international: ***B03D1/016; B03D3/06; C22B3/46;*** **B03D1/004; B03D3/00; C22B3/00;** (IPC1-7): C22B19/26; C25C1/16

- European: B03D1/016; B03D3/06; C22B3/46

Application number: CA19810375490 19810414

Priority number(s): DE19803014315 19800415; DE19813104578 19810210

Also published as:

- FI811152 (A)
- ES8203107 (A)
- DE3104578 (A1)

Abstract of **CA1180195**

A method for removing metals from metal-salt solutions, more particularly for purifying neutral zinc liquors for electrolysis by cementation in a vibrating reactor and subsequent separation of the cementate from the purified solution, characterized in that the separation is carried out in a high speed separating device.

Consumer and Corporate Affairs Canada
Consommation et Corporations Canada

(11) (A) No. 1 180 195

(45) ISSUED 850102

(52) CLASS 53-377
C.R. CL. 23-415

(51) INT. CL. [3] C22B 19/26, C25C 1/16

(19) (CA) CANADIAN PATENT (12)

(54) Method and Apparatus for Removing Metals from Metal-Salt Solutions

(72) Fischer, Holger;
Rachor, Frank;
Esna-Ashari, Mohammed;
Paternoga, Paul;
Doll, Manfred;
Hillmann, Gerd,
Germany (Federal Republic of)

(73) Granted to Klöckner-Humboldt-Deutz Aktiengesellschaft, Germany (Federal Republic of)

(21) APPLICATION No. 375,490

(22) FILED 810414

(30) PRIORITY DATE Germany (Federal Republic of)
(P 30 14 315.8) 800415 Germany (Federal Republic of)
(P 31 04 578.2) 810210

No. OF CLAIMS 7

Canada

ABSTRACT OF THE DISCLOSURE

A method for removing metals from metal-salt solutions, more particularly for purifying neutral zinc liquors for electrolysis by cementation in a vibrating reactor and subsequent separation of the cementate from the purified solution, characterized in that the separation is carried out in a high speed separating device.

This invention relates to a method and an apparatus for removing metals from metal-salt solutions, more particularly for purifying neutral zinc, liquors, lyes, leaches for electrolysis, by cementation in a vibrating reactor and subsequent separation of the cementate from the purified solution.

The metal-salt solution, or neutral zinc liquor, arising during the leaching of calcined zinc-blende concentrate for example, contains, in addition to dissolved zinc-sulphate, other valuable metals which have passed into solution, such as copper, cobalt, nickel and cadmium. Direct use of the neutral zinc-liquor for electrolytic separation of zinc is not possible, in that the electrochemically nobler impurities CU, Co, Ni, Cd etc. are separated cathodically with the zinc, which considerably impairs the quality of the cathode. At the same time, the current efficiency may be substantially reduced by a drop in hydrogen overload. The additional metals in the metal-salt solution constitute impurities and must be eliminated prior to further processing.

There are four main methods of purifying metal-salt solutions: chemical precipitation, electro-chemical separation, ion-exchange (solvent-extraction), and cementation, and these methods may also be combined.

The technical journal "Erzmetall" 31 (1978) discloses, on pages 170 to 175, a method whereby unpurified neutral zinc liquors are treated by multi-stage cementation in a vibrating reactor, the separation of the cementate from the purified solution by filtration through filter-presses.

Cementation experiments in a vibrating reactor with preciptants in granular form have indicated that even after very short periods of residence of only 2 minutes, for example, the cementation has advanced to an extent such that

the copper, nickel and cobalt contents in the purified solution are below 0,1 milligrams per litre, while the cadmium content drops to 0,2 milligrams per litre. The substantial acceleration of the cementation process, arising from the use of a vibrating reactor appears, however, to be a disadvantage during subsequent separation of the cementate from the purified solution by filtration in a filter-press, since a major part of the precipitated metal-cement may pass into solution again. This is caused on the one hand by the lengthy period of residence of the cementate in the filter-presses. On the other hand, the accelerated cementation in the vibrating reactor causes the cementate to redissolve distinctly faster. As an explanation for this , it may be assumed that the cementation conditions have a substantial effect upon the way in which the cementate crystallizes and therefore also upon the redissolving properties. The use of filter-presses for separating the cementate from the purified solution also has the disadvantage that the gel-like zinc-hydroxides $Zn(OH)_2$ or other metal hydroxides formed, such as $Ni(OH)_2$ or $Cd(OH)_2$ rapidly render the filters unserviceable by their adhesive action.

It is therefore the purpose of the invention to indicate a method and an apparatus for removing metals from metal-salt solutions which largely prevents redissolving of the metal cement or cementate once it has been formed and, at the same time, impedes reoxidizing of the cementate by contact with oxygen, improves the separation of the cementate from the purified solution, and optimizes the process as a whole from the economic point of view.

According to the invention, this purpose is achieved by carrying out the separation in a high-speed separating device. This provides a technical teaching for the purification

of neutral zinc liquors for example, for purposes of electrolysis, in a particularly economical and simple manner, using a multi-stage method.

According to one advantageous embodiment of the invention, the average time during which the purified solution is in contact, in the high-speed separating device, with the recementate does not exceed 5 minutes. This reduces the redissolving of cementate to within economically acceptable limits.

Another advantageous configuration of the invention makes use of a centrifuge as the high-speed separating device, adding a flocculant for coagulation purposes. The use of a centrifuge, for example a helical conveyor centrifuge with a solid casing for separating the cementate from the purified solution, in conjunction with the use of strongly anion-active flocculants, makes it possible to adjust the average period of residence of the purified solution to less than 5 minutes, with very efficient separation, as compared with known filter-presses in which the average period of residence of solids is normally about 8 to 10 hours. As compared with the known state of centrifuging technology, it is surprising to note that almost complete separation of the cementate from the purified solution is obtained. The use of a helical-conveyor centrifuge with a solid casing offers the further advantage that the moisture content of the residue therein separated is very low as compared with conventional processes, being less than 30%.

For example, a purified solution ready for use has the following composition: $<0,2$ mg/l of Cu, $<0,4$ mg/l of Cd, $<0,1$ mg/l of cobalt and $<0,05$ mg/l of Ni.

According to another configuration of the invention, it is considered expedient to carry out the high-speed

separation in a rotary filter press or a pressure filter, both with continuous solids discharge. With an appropriate filter medium this also ensures complete separation of the metal gels and metal hydroxides such as $Zn(OH)_2$, $Co(OH)_2$, $Cd(OH)_2$ and $Ni(OH)_2$. Thus a solution having a high degree of purity may be obtained in a single purifying stage.

In one desirable configuration of the invention, the purified solution is passed to a post-cementation device followed by a filtering unit. This arrangement provides a maximal degree of purity for purposes of electrolysis, for example: 0,05 mg/l of Cu, 0,15 mg/l of Cd, 0,98 mg/l of Co and 0,05 mg/l of Ni.

Since the purified solution emerging from the high-speed separating state is very clean, the post-cementation device, and the subsequent filtering unit, constitutes a fine-purifying stage requiring little expenditure for costly cementation agents, for example zinc-dust.

According to another advantageous configuration of the invention, the residue from the filtration stage is mixed with the metal-salt solution before reaching the vibrating reactor. Since this residue contains a considerable amount of zinc, the use thereof increase the yield of zinc from the process as a whole, thus substantially improving the economics of the method.

In another desirable configuration of the invention, post-cementation is carried out in a vibrating reactor which provides the known advantages of satisfactory control of the conduct of the process, high throughput and compactness.

Another advantageous configuration of the method according to the invention, using a centrifuge as the high speed separating device and suitable flocculant for co-agulation, consists in that the flocculant contains an

acrylamide polymer having a molecular weight of between 1×10^6 and 30×10^6, preferably 15×10^6 g/mole, and in that the flocculant is prepared in the form of an 0,01 to 0,2, preferably an 0,1%, solution, between 5 and 25, preferably about 7, mg/l being added to the liquor.

The use of this agent, comprising particularly long-chain molecules, provides, surprisingly enough, almost complete separation of the neutral liquor from the high-solids-content sludge-phase containly mainly metallic solids from the cementation products, with no detrimental re-dissolving. The purpose of obtaining accurate separation of the two phases, and overcoming existing difficulties and limitations, is thus achieved. In this connection it is surprising to note that optimal results are obtained with the special form of conditioning and metering.

Further improvement is obtained, according to another proposal, by carrying out the cementation in the vibrating reactor at a temperature of between 85 and 95, preferably 92°C, with an addition of between 6 and 15, preferably 6 mg/l of antimony-trioxide, and in that the precipitant used is zinc granules in a grain-size of between 3 and 30, preferably 10 mm.

It is furthermore proposed to use as the centrifuge a helical-conveyor centrifuge with a solid casing operating in the range between 600 and 1200, preferably about 900g in uniflow, the liquor being stirred vigorously, after separation of the cementate, in passing through an intermediate container, with an addition of chamber-cell acid and with an addition of between 0,1 and 0,7, preferably 0,3 g/l of zinc-dust, and being adjusted to a pH value of between 3 and 5, preferably 4,5, with a period of residence of preferably 15 minutes.

Operating the solid-casing centrifuge at 900 g

produces a gravitational field with sufficiently high acceleration within range of which separation may be carried out with relatively short periods of residence, for example between 1 and 2 min. Thus the cementation products to be separated, especially under the protection of the unusually long-chain flocculant which keeps them moist, have no opportunity to redissolve. Furthermore, a satisfactory discharge of solids is assured by the worm through the conically tapered part of the centrifuge casing.

According to still another configuration of the invention, the apparatus also comprises a post-cementation device, preferably a vibrating reactor, the outlet end of which is connected to a filtering unit. This ensures maximal possible safety and electrolyte quality.

The invention may also be improved, with advantage, by arranging the high-speed separating device below the vibrating reactor which supplies it, and by connecting it, through pipelines, either directly or through a settling tank, to the feed-pipe to the said high-speed separating device. According to the invention, this arrangement eliminates the need for a delivery pump between the cementation device and the separating device, thus reducing costs.

Thus, in one aspect of the present invention, there is provided a method for removing metals from metal-salt solutions, more particularly for purifying neutral zinc-liquors for electrolysis by cementation in a vibrating reactor and subsequent separation of the cementate from the purified solution, characterized in that the said separation is carried out in a high-speed separating device.

Thus, in a further aspect of the present invention there is provided an apparatus for carrying out a method for removing metals from metal-salt solutions, more particularly

for purifying neutral zinc liquors for electrolysis, by cementation in a vibrating reactor and subsequent separation of the cementate from the purified solution, wherein the said separation is carried out in a high-speed separating device, said apparatus characterized in that a high-speed separating device, preferably a solid-casing helical-conveyor centrifuge is connected to the vibrating reactor.

In one aspect of the present invention, there is provided a method for the purification of a zinc salt solution to make it useable in an electrolytic cell for the recovery of zinc which comprises; subjecting the solution to cementation in an oscillating reactor at a temperature between 85° and 95°C with the addition of from 6 to 15 mg/l of antimony-trioxide together with a granular precipitant comprising zinc particles having a particle size range of from 3 to 30 mm, passing the cementation reaction product into a cylindrical-conical helical conveyor centrifuge operating in the range from 600 to 1,200 g, adding a flocculating agent to the reaction product in the centrifuge, the flocculating agent being an acrylamide polymer having a molecular weight between 1 million and 30 million, the flocculating agent being added to the reaction product in the form of 0.01 to 0.2% solution in the amount of from 5 to 25 mg/l, maintaining the reaction product in the centrifuge for a period of time less than 10 minutes, and recovering a purified solution from the centrifuge.

In a still further aspect of the present invention, there is provided an apparatus for the purification of a metal salt solution to make it useable in an electrolytic cell which comprises, an oscillating reactor, means for introducing the salt solution and a cementation medium into the oscillating reactor, a centrifugal separator receiving the discharge from the oscillating reactor, liquid discharge means

for withdrawing a purified liquid from the centrifugal separator, slurry discharge means for withdrawing a cementate from the centrifugal separator, a second oscillating reactor receiving the discharge from the slurry discharge means for further cementation, and a filtration device receiving the output from the second oscillating reactor.

In a still further aspect of the present invention, there is provided a method for removing metals from metal-salt solutions, more particularly for purifying neutral zinc liquors for electrolysis by cementation in a vibrating reactor and subsequent separation of the cementate from the purified solution, characterized in that the separation is carried out in a high speed centrifuge, a flocculant is used for coagulation and the flocculant contains an acrylamide polymer having a molecular weight of between 1×10^6 and 30×10^6 g/mole, that the flocculant is prepared as a 0.01 to 0.2% solution, and is added to the liquor in an amount of between 5 and 25 mg/l.

In a still further aspect of the present invention, there is provided an apparatus for carrying out a method for removing metals from metal salt solutions, including for purifying neutral zinc liquors for electrolysis, by cementation in a vibrating reactor and subsequent separation of the cementate from the purified solution, wherein the separation is carried out in a high speed separating device, the apparatus characterized in that a high speed separating device, comprising a solid casing helical conveyor centrifuge is connected to the vibrating reactor.

Further details, characteristics and advantages of the invention may be gathered from the following explanation of a plurality of examples of embodiment of the apparatus for the execution of the method according to the invention, in conjunction with the drawings attached hereto, wherein:

Figure 1 shows an installation for single-stage purification of zinc-liquor for electrolysis;

Figure 2 is another representation of zinc-liquor purification with main- and after-purification stages;

Figure 3 is a representation as in Figure 2 with a vibrating reactor in use in the after-purification stage.

The installation illustrated in Figure 1, with the apparatus according to the invention for the execution of the method, comprises, as its main components, a vibrating reactor 1 and a high-speed separating device 2 and, as secondary components, a feed-hopper 3 and a settling tank 4, the said units being connected together by pipelines 5, 6 and 7. Vibrating reactor 1 comprises two tubes 8, 9 which are caused to vibrate in circles by a longitudinally arranged out-of-balance drive. Located at the ends of the said tubes are slotted discs 10, 11. High-speed separating device 2 is shown in the form of a solid-casing helical-conveyor centrifuge having a drum-casing 12 and a conveyor-worm 13; it comprises a feedpipe 14, a liquid outlet 15, and a residue outlet 16. Feed-hopper 3 is equipped with an agitator 17

and a heating-coil 18. Pipelines 5, 6 contain pumps 19 and control-valves 20.

When the installation according to Figure 1 is in operation, the feed-hopper contains a metal salt solution 21, known as the raw liquor and containing, for example 150 g/l of Zn, 800 mg/l of Cu, 500 mg/l of Cd, 10 mg/l of Co and 20 mg/l of Ni. Cementation aids 22 are in the form of additions such as antimony-tartrate or also Sb_2O_3, the amounts used being such as to maintain an approximately constant antimony concentration of 20 mg/l in purified solution 23 at the outlets from tubes 8,9 of the said vibrating reactor.

Heating coil 18 raises the temperature of the raw liquor in hopper 3 to about 90 to 95°C. At a pH value of between 3 and 4, 5 raw liquor 21 is fed through line 5, by the action of pumps 19, to tubes 8, 9 of the vibrating reactor. The throughput, and the level of the liquid, in the vibrating reactor, are controlled by pumps 19 and regulating valves 20. Located in tubes 8, 9 of the said vibrating reactor is cementation agent 24 which is fed continuously thereto by a metering element 25. In the present case, the cementation agent used is zinc granules having a diameter of about 10 to 15 mm, the amount introduced being such that tubes 8 and 9 are between 60 and 90% full. A granular zinc-antimony alloy may also be used as the cementation agent in order to introduce the desired amount of antimony, as indicated above, into the purified solution.

Purified solution 23 leaves vibrating reactor 1, together with the centrate and the zinc particles, through line 6, cementation agent 24 being held back by slotted discs 10, 11 and reaches settling tank 4 where the coarse solid material is precipitated as a settling residue 26 which is then mixed, continuously or intermittently, with the raw

liquor in line 5, or may be withdrawn from time to time for other purposes. The purified solution, with cementate 27 suspended therein, passes through line 7 into feed-pipe 14 to high-speed separating device 2, for example a solid casing helical conveyor centrifuge. A flocculant 28 is mixed with purified solution 27 before it is introduced into the separating device. Separation residue 29 leaves the said separating device through residue-outlet 16 and contains solids of a grain size of up to 1 μm. The said separation residue may be processed, by known methods, for recovering non-ferrous and noble metals. Purified solution 30, freed from solids, contains $<$0,2 mg/l of copper, $<$0,4 mg/l of cadmium, $<$0,4 mg/l of cobalt and $<$0,05 mg/l of nickel at a pH value of 5,5 and may therefore be used in a large number of plants for the recovery of zinc by electrolysis.

In order to produce cathod-zinc 40, purified solution 30 may be fed, for example, by means of a delivery pump 31, to a storage and test tank 32 from which an electrolyzing tank 33 is fed, wherein chamber-cell acid 34 is mixed with other additives 35 to form a serviceable electrolyte 36. This is then fed to a cooling tower 37 to which a blower 38 is connected.

Cooled electrolyte 36 flows continuously to electrolysis cell 39 wherein zinc is separated cathodically as cathode zinc 40.

In the example described, high-speed separating device 2 may also be replaced by a rotary-filter-press or pressure-filter comprising means for the continuous removal of separation-residue 29, in order that the average contact time between the purified solution and the cementate in the said separating device may be as short as possible, in order to prevent the cementate already formed from re-dissolving.

The installation illustrated in Figure 2 comprises, in addition to the main purification stage shown in Figure 1, an after-purification stage consisting of a post-cementation device in the form of an intermediate container 41 and a filtration device 42, for example, which are connected together by a line 43 in which is located a delivery pump 44 and a pH-value control. Intermediate container 41 comprises an agitator 46 and is connected through line 47 to high-speed separating device 2.

When the installation is in operation, purified solution 30 passes from high-speed separating device 2, through line 47, into intermediate container 41, into which, for the purpose of after-purifying the said purified solution, a cementation-agent, for example zinc-dust 48 must be metered simultaneously in small amounts only, for example 500 g/l. In order to adjust the pH value to between 4 and 4,7, a suitable amount of chamber-acid 49 is also supplied by pH control 45 to the said intermediate container. Separation of the cementate formed in the after-purification stage from after-purified solution 50 intended for electrolysis is effected in a suitable filtration device 42, for example a filter-press, filtrate 50 from which is fed to the after-purified solution for the purpose of recovering zinc from the electrolysis treatment, whereas filter-residue 51, which is very rich in zinc, is mixed with metal-salt solution 21. It is therefore desirable for filtration device 42 to be connected, by lines 52 and pump 53, to line 5 for introduction into vibrating reactor 1.

According to Figure 3, a second vibrating reactor 54 is used, with advantage, as the post-cementation device, cementation-agent 54, for the after-purification of zinc liquors, being fed thereto also in the form of zinc-granules.

For the purpose of adjusting the pH value in pH control 45, chamber-acid 56 may be introduced into line 57 through which a pump 31 delivers purified solution 30 from high-speed separating device 2 to the said second vibrating reactor. As a result of the extent to which solution 30 is pre-purified, the throughput in vibrating reactor 54 is between four and five times that in first vibrating reactor 1. Filtrate 50, or the after-purified solution supplied for electrolysis, has the following contents, for example: 0,05 mg/l of Cu, 0,15 mg/l of Cd, 0,08 mg/l of Co, and 0,05 mg/l of Ni.

The method and apparatus according to the invention may be used not only as indicated in the foregoing examples, but also for removing from metal-salt solutions other metals not mentioned here. This applies in principle to all cementation-processes used to purify, recover or separate metals from metal-salt solutions. An important prerequisite is the use of suitable active substances for the apparatus, especially as regards resistance to corrosion. By way of example, it is pointed out that use of the method and apparatus according to the invention makes it possible:

a) to separate nickel by means of cobalt or cobalt and sulphur from sulphuric cobalt-nickel-containing solutions;

b) to precipitate from chloridic solutions, for example Co, Ni, Cu, Ag and Au with zinc or iron as the cementation-agent;

c) to cementate gold and/or silver out of cyanide solutions by means of zinc, and

d) to cementate copper out of copper-containing mine waters.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for the purification of a zinc salt solution to make it useable in an electrolytic cell for the recovery of zinc which comprises; subjecting said solution to cementation in an oscillating reactor at a temperature between 85° and 95°C with the addition of from 6 to 15 mg/l of antimony-trioxide together with a granular precipitant comprising zinc particles having a particle size range of from 3 to 30 mm, passing the cementation reaction product into a cylindrical-conical helical conveyor centrifuge operating in the range from 600 to 1,200g, adding a flocculating agent to said reaction product in said centrifuge, said flocculating agent being an acrylamide polymer having a molecular weight between 1 million and 30 million, said flocculating agent being added to said reaction product in the form of a 0.01 to 0.2% solution in the amount of from 5 to 25 mg/l, maintaining said reaction product in said centrifuge for a period of time less than 10 minutes, and recovering a purified solution from said centrifuge.

2. A method according to claim 1 which includes the step of:

subjecting said purified solution to an additonal cementation and;

filtering the product of said additional cementation.

3. A method according to claim 2 which includes the steps of:

combining the filter residue with said metal salt solution prior to introducing the same into said oscillating reactor.

4. A method according to claim 2 in which:
said additional cementation is also carried out in an oscillating reactor.

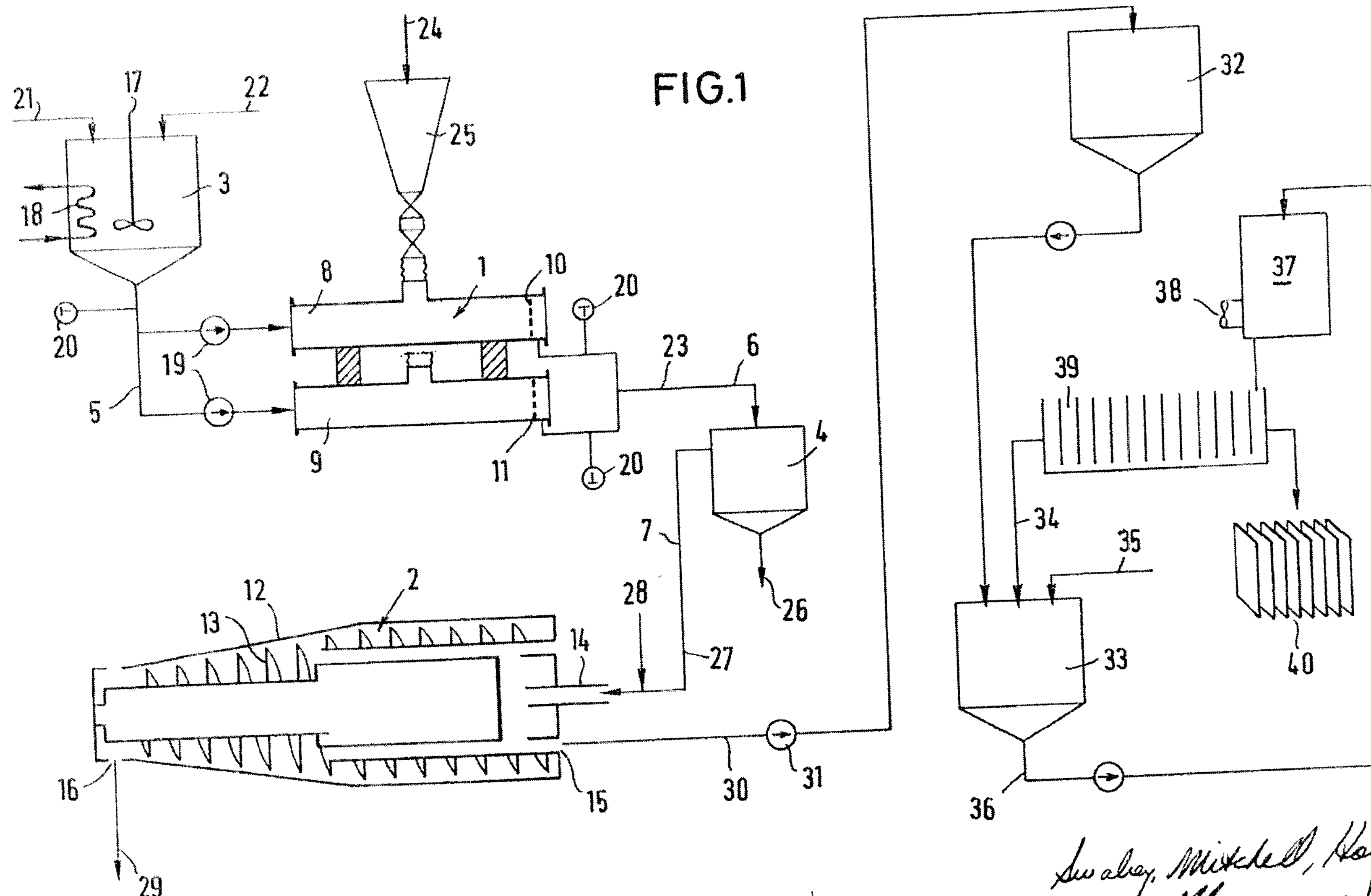
5. A method according to claim 1, including the step of providing said centrifuge in the form of a solid casing centrifuge operating in uniflow.

6. A method according to claim 1, wherein after separation of cementate, the liquor is stirred intesively in passing through an intermediate container, with the addition of chamber-cell acid and with the addition of zinc dust in an amount of between 0,1 and 0,7, preferably 0,3 g/l and, during a period of residence of preferably 15 min., is adjusted to a pH value of between 3 and 5.

7. An apparatus for the purification of a metal salt solution to make it useable in an electrolytic cell which comprises; an oscillating reactor, means for introducing said salt solution and a cementation medium into said oscillating reactor, a centrifugal separator receiving the discharge from said oscillating reactor, liquid discharge means for withdrawing a purified liquid from said centrifugal separator, slurry discharge means for withdrawing a cementate from said centrifugal separator, a second oscillating reactor receiving the discharge from said slurry discharge means for further cementation, and a filtration device receiving the output from said second oscillating reactor.

3-1

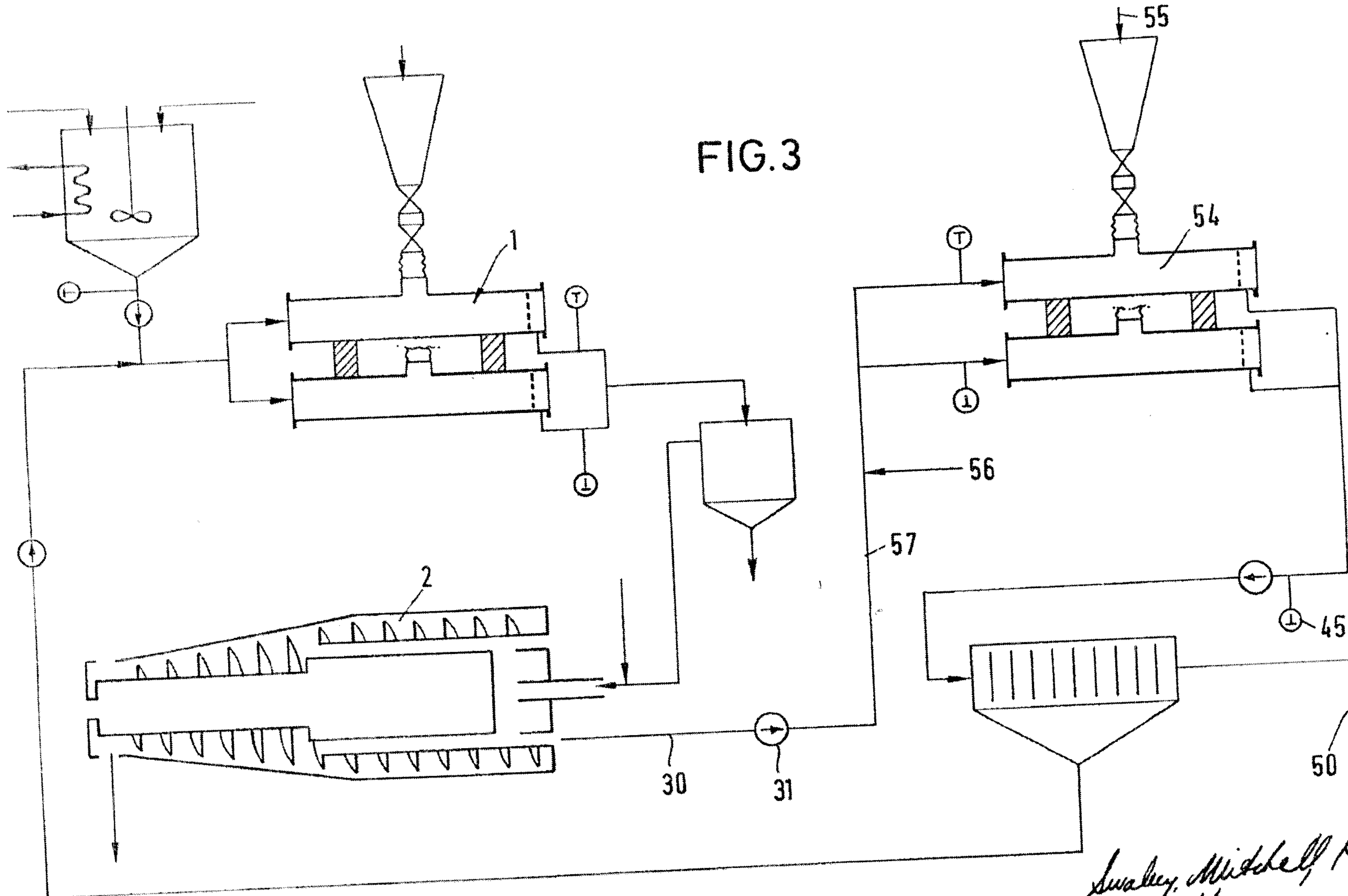
FIG.1



Swabey, Mitchell, Houle
Marcoux & Sher
PATENT AGENTS

1180195
3.3.

FIG.3



Swabey, Mitchell, Houle
Marcoux & Sher
PATENT AGENTS